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Final Report for period ending February 18, 1982  
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Development of Critical Molecular Weight-Property  
Specifications for High Performance Polymers Used  
as Adhesives and Composites

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Abstract: This report consists of 3 parts

Part A: The polyimide resin, LARC-160, has been prepared from diethyl-3, 3',4,4'-benzophenone tetracarboxylate (BTDE), ethyl-5-norbornene-2,3-dicarboxylate (NE) and Jeffamine AP-22. The imidization reactions of NE and BTDE have been studied by HPLC,  $^{13}\text{C}$ -NMR and IR. NE imidizes slowly at 12°C; BTDE imidizes when the resin is heated above 100°C. Both imidization reactions proceed directly to the imide. Neither amic acid is present in significant quantities at any stage of the imidization reactions. The monomer mixture has been stored at 12°C for periods up to 14 months. The effects of resin aging at this temperature on the chemical composition of the resin monomer mixture and the imidized polymer formed on curing have been investigated. Aging the resin monomer mixture has the effect of partially advancing the imidization reaction. The average size of the cured polymer increases slightly with resin age.

Part B: The stability of a series of BTDA-DABP and BTDA-MDA, polyimide precursor resins in DMAC was investigated by measuring their molecular weight measurements were made using a membrane osmometer. The dependence of the rate of degradation on the chemical nature of the isomeric diamine and the geometric structure about the amide linkage was examined and discussed in terms of a previously proposed mechanism for degradation. The effect of the presence of water, the concentration of the resin, and the temperature was also investigated. The degradation rate was doubled by the addition of 0.5(v/v) %  $\text{H}_2\text{O}$  to the anhydrous resin solution. Increasing the concentration of the resin solution and the presence of an electron donating group between the phthalic acid groups increased the stability.

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Part C: Glass transition temperature and the solubility of crosslinked nadic polyimides were examined for two systems. The first was solventless LARC-160, and the other was PMR. Both the PMR and LARC-160 resins were used as received from the NASA Langely Research Center. Both of these resin systems consist of a mixture of the diethyl ester of benzophenone tetracarboxylic acid (BTDE), and the ethyl ester of norbornene dicarboxylic acid (NE) and methylene dianiline (MDA). The LARC-160 differs from the PMR resin in that LARC-160 contains, in addition to bifunctional MDA isomers, trifunctional aromatic amines.

## Part A

Characterization of the Imidization of the  
Aromatic Polyimide, LARC-160

By

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Introduction

Polyimides with aromatic groups in their backbone have generated considerable interest as matrix resins for high performance composites because of their thermal and thermooxidative stability.<sup>1</sup> On the other hand, the high glass transition temperatures of polyimides make processing difficult. One processing approach has been to make a predominately linear polyamic acid resin and then to imidize the polymer chain in the cure cycle. A second and more promising approach is to make relatively short imide chains which are encapped with a nadic group.<sup>2</sup> These oligomeric chains are then crosslinked in the post-cure cycle through an addition reaction of the end-capping groups at a higher temperature and pressure. LARC-160 is prepared in this manner. Diethyl-3,3',4,4'-benzophenone-tetracarboxylate, ethyl-5-norbornene-2,3-dicarboxylate (nadix ester) and a mixture of amines composed primarily of p,p'-methylenedianiline are mixed and cured at a temperature between 140 and 200°C, to form the imide. At higher temperatures and pressures, these imide oligomers are crosslinked through an addition reaction involving the nadic end-capping group.

In a preliminary study, Young and Sykes reported that aging the resin at room temperature affected the mechanical properties of cured LARC-160.<sup>3</sup> We

have examined the effects of resin aging at 12°C on the chemical composition of the resin monomer mixture and the imidized polymer formed on curing. Changes in the chemistry of the monomer mixture with age have been observed and characterized by HPLC and  $^{13}\text{C}$ -NMR. The effect of resin age on the size of the polyimide oligomers, which determines the distance between crosslinks, has been determined by HPLC. The imidization reactions of the nadic and benzophenone tetracarboxylate monomers have been studied using HPLC,  $^{13}\text{C}$ -NMR, and IR. A revised reaction scheme for LARC-160 polymerization has been proposed.

### Experimental

The solventless LARC-160 resin was prepared as prescribed by St. Clair and Jewell using 3,3',4,4'-benzophenone tetracarboxylic anhydride (BTDA), 5-norbornene-2,3-dicarboxylic anhydride (NA) and a commercially available mixture of aromatic amines, Jeffamine AP-22, which is composed primarily of p,p'-methylenedianiline (MDA),<sup>2</sup> (see Fig. 1). BTDE, the diethylester of BTDA, was prepared by dissolving the anhydride in a 5 M% excess of ethyl alcohol and refluxing for one hour. NE, the monoethyl ester of NA was similarly prepared. These mixtures were then cooled and mixed with the appropriate amine molar equivalent of Jeffamine AP-22. The resulting resin mixture was stored in a refrigerator at 12°C.

High Pressure Liquid-Gel Permeation Chromatography (HPLC-GPC) was performed on a Waters' Associates Liquid Chromatograph equipped with a model M-6000A chromatography pump, model U6K injector, and a Model E 401 differential refractometer.

Two column-solvent systems were used: (a) samples were dissolved in tetrahydrofuran (THF), UV grade, from Burdick and Jackson, then eluted on a

four column bank consisting of two 500 Å° and two 100 Å° µ-styragel columns, or (b) samples were dissolved in UV grade chloroform, also from Burdick and Jackson, and eluted on a five column bank consisting of a 10<sup>3</sup> Å°, two 500 Å° and two 100 Å° µ-styragel columns.

Carbon 13 Nuclear Magnetic Resonance (<sup>13</sup>C-NMR) studies were done on a Varian FT-80A NMR Spectrometer. Samples of the resin were dissolved in DMSO-d<sub>6</sub>, with TMS as an internal standard. A spectral width of 5000 Hz was used.

<sup>13</sup>C chemical shift assignments of the carbonyl resonances of BTDE and NE were made by comparison with the monomers and the following model compounds: 3-[(phenylamino)carbonyl]-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; 2-[(phenylamino)carbonyl]-benzoic acid; N-phenyl-5-Norbornene-2,3-dicarboximide; N,N'-(methylenedi-p-phenylene)di-5-norbornene-2,3-dicarboximide (Bisnadimide or BNI); and p,p'-methylenedianiline (MDA). These compounds were supplied by NASA-Langley Research Center.

A Perkin-Elmer 337 Grating Infrared Spectrophotometer was used for IR studies. Films of fresh resin were prepared on KBr plates and the same sample was taken through a given cure cycle. IR spectra were taken of the fresh resin and at selected points along the cure cycle.

## Results

### Effect of Age on the Resin Monomer Mixture

The freshly prepared monomer resin mixture was stored at 12°C in air. Aging of the resin was monitored by HPLC. (Fig. 2, Table I.) Peaks were assigned according to the elution volumes of the respective monomeric species and verified by spiking resin samples with the monomer. Weight %'s were corrected for differences in the differential refractive index as a function of

concentration for each monomer species. A composite value for the oligomers was estimated based on the experimentally determined values for the monomers.

As can be seen in Table I, the nadic group reacted with time, even at subambient storage temperatures. The major product of this low temperature reaction was nadimide, the imides formed from the reaction of one MDA with one NE (NI) and one MDA with two NE (BNI). The presence of nadimide was established by comparison of the HPLC spectra of aged resin and a sample enriched with NI + BNI. Nadimide was first observed in four week old resin and continued to increase in quantity with resin age throughout the study until, after 377 days at 12°C, all of the nadic groups had imidized. (Table I.) <sup>13</sup>C-NMR data which are presented below also show that after 14 months virtually all of the nadic groups are imidized.

In contrast to NE, BTDE did not imidize at 12°C. An exact determination of the change in the weight % of BTDE was made difficult because the trifunctional amine in Jeffamine (peak 3.5) eluted as a shoulder on the BTDE peak (peak 4). Complete separation of the two components was not possible on the four columns used. Measurement of the relative contribution of each of these two components was subject to error as shown by the variation in weight % reported for these two species. Determining the area of the BTDE peak was further complicated by the presence of the amic acid of the nadic monomer which eluted at about this volume. Additionally, some of the lower molecular weight imides formed by the reaction between one NE and the tri-(n=1) or tetra-(n=2) functional Jeffamine overlap and increasingly contribute to this peak area with resin age.

A low molecular weight imide (peak 5) was formed when the resin monomer

mixture was prepared. Its weight percent increased with time. The low molecular weight imide is thought to be a mixture of higher molecular weight reaction products between the nadic ester and the tri- and tetrafunctional amines (for example,  $\text{NE}_2\text{-Jef.}$ ,  $n=2$ ). Evidence will be presented later that these short imides are incorporated into longer chains during curing.

The data presented above were obtained on monomers mixed at  $-50^\circ\text{C}$ , the temperature at which Jeffamine is just fluid enough to ensure proper mixing with the esters. When warmer mixing temperatures were used ( $>80^\circ\text{C}$ ) a monomer resin mixture resembling aged, "cold-mixed" resin was obtained (Fig. 3, Table III). In fact, about the same degree of nadic imidization, as measured by nadimide formation, was observed in the "warm-mixed," day old monomer resin mixture as in the aged "cold-mixed" resin which had been stored eight months. The warm mixed resin also contained more of the low molecular weight imide (peak 5). The weight % of BTDE remained at or above its originally formulated value of 33% supporting the view that little if any of it had reacted. (The apparent increase in the weight % of BTDE was likely due to formation of the amic acid of the nadic group and nadic-jeffamine imides which elute at the same volume.)

These marked differences in the apparent extent of reaction of "warm-" and "cold-" mixed resin show that the monomer resin mixture is sensitive to preparation and storage conditions. For composite preparation, the resin is warmed slightly to achieve proper impregnation of the composite fibers. The actual time and temperature of this prepregging operation can apparently have an effect on the extent of the reaction or "age" of the resin and on resin properties in subsequent curing steps.

In order to examine the imidization reaction of the LARC-160 resin more



explicitly, a  $^{13}\text{C}$ -NMR study of the carbonyl absorption peaks of the aging resin was undertaken. A fresh batch of resin was prepared and mixed with both esters and amines at  $80^\circ\text{C}$ . Samples of this resin were dissolved in  $\text{DMSO-d}_6$  at different ages for  $^{13}\text{C}$ -NMR analysis.

As can be seen in Fig. 4, examination of the nadic carbonyl resonances indicates that nadimide (177 ppm), designated (a), was present even in this initial sample. The nadic ester and acid peaks (173.3 and 172 ppm), (b and c) were also present. No nadic amide (169.8 ppm), (d), could be observed. However, after six days at  $12^\circ\text{C}$  (Fig. 5) a small but distinct amide peak (d) was observed. The magnitude of this peak remained small and disappeared after 14 months of storage at  $12^\circ\text{C}$  when nadimidization was complete (Fig. 6). Thus, while some amic acid is observed as an intermediate, the reaction clearly favors complete imidization. These findings are contrary to the presumed reaction sequence for LARC-160 (Scheme I)<sup>4</sup> which shows the amic acid forming at low temperatures, and the imide appearing only after heat is applied in a dehydration step.

The extent of reaction of the nadic groups with monomer mixture age was determined from the  $^{13}\text{C}$ -NMR data. Although  $^{13}\text{C}$ -NMR does not give quantitative results unless special techniques are employed,<sup>5</sup> an estimate of the amount of nadic carbonyl groups in the acid, ester, amide and imide forms was made. This analysis was possible because we were only comparing quaternary carbons at the same position on the nadic moiety. In this case  $T_1$  and NOE effects on these carbons should be similar, and their relative intensities of about the same magnitude. The extent of reaction was calculated as follows: All carbonyl functional groups were assumed to have the same intensity. Therefore the

fraction of reacted nadic groups was equal to the imide intensity plus twice the amide intensity (one amide carbonyl + one acid carbonyl per molecule in this form) divided by the total intensity of all nadic carbonyl groups. The results are shown in Table II.

Our results on the imidization of the nadic group in aging LARC-160 monomer mixtures substantiate the preliminary findings of Young and Sykes who first reported observing BNI in aging LARC monomer mixtures.<sup>3</sup> Imidization of the nadic group in MeOH solutions of PMR monomers at ambient and 5°C storage temperatures has also been reported.<sup>6</sup> (PMR is a sister resin to LARC in which all of the amine is p,p'-MDA (Jef., n=0)).<sup>7</sup> Neither of these groups were able to fully characterize the nature of the imide nor observed and followed the increase in imidization over an extended period, as is reported here for LARC-160.

The BTDE monomer was monitored in these same <sup>13</sup>C-NMR studies. Unlike NE, BTDE does not imidize under storage conditions. In the warm-mixed LARC monomer mixture, BTDE peaks were observed at 167.7, 167.1, 166.9 and 166.4 ppm, due to the acid and diester in various combinations (Fig. 4 and 5). These resonances neither shifted position nor grew in number with resin age. No peak corresponding to the benzophenone tetracarboxylate imide at 166.2 ppm. was observed at any age. BTDE appears to be stable over the six month storage period of this study. These results are in contrast to the reported slow esterification of BTDE to tri- and tetra-esters reported for PMR.<sup>8-10</sup> One should note, however, that the cold-mixed resin produced spectra which all contained two additional peaks in the benzophenone tetracarboxylate region (Fig. 6). Spectra of a mixture of tri- and tetrafunctional esters prepared in our laboratory also contained the two peaks in question. Quality control studies on the LARC

monomers have shown that small amounts of these esters are often formed during BTDA esterification.<sup>4</sup>

The lack of additional esterification of BTDE in LARC-160 is not too surprising when one compares the monomer mixture with that of PMR. PMR is stored as an alcohol solution of monomers. The degree of tri and tetraester formation has been shown to be a function of the amount of that solvent present.<sup>8</sup> LARC, however, is stored as a neat monomer mixture. Therefore, although a small amount of EtOH should be present as a by-product of the nadic imidization reaction, it is insufficient in quantity to cause BTDE esterification.

Our HPLC and <sup>13</sup>C-NMR studies on the effects of age on the monomer mixture indicate that changes in the monomer mixture with age are confined to reactions involving the nadic group. This group slowly imidizes with time. The BTDE group remains unchanged as indicated by both the HPLC and NMR data.

#### The Imidization of Diethyl-3,3',4,4'-Benzophenonetetracarboxylate

Since the nadic group formed an imide directly and BTDE did not react at low temperatures, the imidization of BTDE was then examined. Was there a distinct polyamic acid stage, or did the BTDE monomer also react directly to form the imide? At what temperature did these reactions take place?

Fresh, "warm-mixed" resin was cured at 180°C. The degree of imidization as a function of cure time at 180° was monitored by both <sup>13</sup>C-NMR to study the cure reaction and by HPLC to monitor oligomer distribution (Fig. 7, Table IV). Within 15 minutes at this temperature the monomers and the low molecular weight imide (peaks 1, 2, 4 and 5) appeared to have reacted. After 15 minutes, changes continued to occur as the shorter oligomers (peaks 6 and 7) reacted to form higher molecular weight polymers. Examination of Fig. 7 shows a gradual shift

in the elution volume of peak 8 to lower values, corresponding to a higher average molecular weight. After 30 minutes of exposure to this cure temperature, material insoluble in THF began to be formed. The amount of this insoluble high molecular weight polymer increased with cure time.

Since BTDE had already completely imidized after 15 minutes at 180°C, this reaction was followed at several lower temperatures to look for the expected amide intermediate in the imidization process. Table V is a summary of the  $^{13}\text{C}$ -NMR results for the carbonyl shifts. In the benzophenone carbonyl region one first observes the disappearance of the ester/acid peaks at 166.9 ppm, (g) and 167.6 ppm, (e), as the amide at 166.3 ppm, (i), and the imide at 166.2 ppm, (j), form. Finally, all peaks in this region (e-i) collapse into the imide peak, (j). The amide peak, (i), is never observed without the simultaneous presence of the imide peak, (j), suggesting that the amide is a transient intermediate in the imidization reaction rather than an isolatable polymeric species.

The fact that imidization of the nadic and benzophenone tetracarboxylic monomers occur at two widely different rates and temperatures was confirmed by IR studies.

An infrared sample was prepared as a thin film between two salt plates. Each sample was run without curing, then the plates were cured for measured amounts of time and additional spectra taken. Once the imide IR absorbance had become constant, the cure temperature was raised on the same sample and the effect of further curing on the sample was observed.

The imide IR absorption peak has been reported to occur between 1810 and 1775  $\text{cm}^{-1}$ .<sup>11</sup> We observed the imide peak at 1790  $\text{cm}^{-1}$  in LARC-160. In the fresh resin the amount of imidization, as measured by the intensity of this peak,

was negligible. As the sample cured, the peak emerged as a shoulder on the broader 1730-1700  $\text{cm}^{-1}$  carbonyl stretch. (Fig. 8.)

The percentage of imidization was calculated using the equation:<sup>12</sup>

$$\text{Percentage Imidization} = \frac{\frac{A(1)}{A(2)}(t) - \frac{A(1)}{A(2)}(t=0)}{\frac{A(1)}{A(2)}(t=\infty) - \frac{A(1)}{A(2)}(t=0)}$$

$A(1)$  = Absorbance of Imide Peak at 1790  $\text{cm}^{-1}$

$A(2)$  = Absorbance of Standard Reference Peak at 1490  $\text{cm}^{-1}$

$t = \infty$  was taken as the time beyond which no further changes in the imide peak were observed at 220°C.

No imidization was observed in the resin before ~~heating~~. When the sample was heated at 70°C for up to 660 minutes, the imide peak grew to approximately 40% of its final size. The sample was then heated at 180° for up to 360 minutes. This second cure stage brought about a significant increase in the amount of imidization, to approximately 85% of the final imidization. The sample was then cured at 220°C for up to 330 minutes. The amount of imidization increased slightly indicating that the imidization reaction was not quite complete after curing at 180°C. (Table VI.) As shown in Table VI, slightly less than 1/2 of the imide is formed below 100°C, consistent with the hypothesis that only the nadic group, which represents 48% of the carbonyl carbon in the monomer mixture, is reacting at this lower (70°) temperature. The remainder of the imidization, which involves BTDE, takes place at the higher temperature, (180°).

An absorption band at 1850  $\text{cm}^{-1}$  at temperatures  $\geq 120^\circ\text{C}$  has been reported and attributed to anhydride formation as an initial competing reaction to imidization in the related PMR system.<sup>13-15</sup> We do not observe any absorbance

in this region for the curing LARC resin. Furthermore, the  $^{13}\text{C}$ -NMR experiments on samples cured at  $180^\circ$  did not detect any anhydride for either the nadic (172.3 ppm) or benzophenone tetracarboxylate (162.4 ppm) carbonyl groups. (Table V.)

The IR experiments substantiate the  $^{13}\text{C}$ -NMR and HPLC data which indicate that imidization occurs in two stages: first, low-temperature imidization of the nadic moiety forming the end-capped amines and bisnadimide, and second, at temperatures over  $100^\circ\text{C}$ , imidization of the benzophenone tetracarboxylate monomer occurs.

In solution, polyimides are formed via the low temperature polymerization to the polyamic acid, which imidizes upon the application of heat. Polymerization of solventless LARC monomeric resin has been assumed to follow the same reaction sequence.<sup>4</sup> However, based on the above evidence for the formation of bisnadimide, even at subambient temperatures, and the observation of the benzophenonetetracarboxyl amic acid only as a transient intermediate, we believe Scheme II is a more accurate representation of the imidization reaction sequence for LARC-160 polymerization.

#### The Effect of Resin Age on the Cured Polymer

The major effect of age on the LARC-160 monomer mixture appears to be the preferential reaction of NE with the amine mixture. The consequences of this partial advancement on the cured resin product will be considered next.

The effect of resin aging on the length of the oligomeric chains was examined. Curing reactions under constant conditions were performed at intervals as the "cold-mixed" LARC-160 monomer resin mixture aged. Samples of the aging monomer resin mixture were cured at either  $140^\circ$  or  $180^\circ$  for one hour on the same day that

the monomer mixture was examined by HPLC.

As can be seen by Fig. 9 and Table VII, HPLC analysis of the polymeric species formed at 180° shows a small but noticeable shift toward higher molecular weight as the resin ages. The elution volumes of the three polymeric segments designated Polymer 1, 2 and 3 correspond to elution volumes for polystyrenes of molecular weight 1000, 3000-20,000 and >20,000 respectively. Peak 5, which has been attributed to unfully endcapped imides (see discussion of monomer mixture results) is not present in these cured samples, and the weight % of peak 3, which was attributed to BNI + NI is reduced. During the curing process, the unfully endcapped nadimides are incorporated into longer chains. BNI, capped at both ends, is unable to react further, and remains as a low molecular weight component in the polymer system. BNI is observed as a major reaction product in the cured polymer regardless of resin age. Results for ages greater than 106 days are not shown because the amount of insoluble material increased with age so that these polymers could not be examined by the solution methods available to us.

A similar shift toward higher molecular weight of the cured product with increasing monomer mixture age is observed at a 140° cure temperature. Changes in the polymer cured at 140°C for one hour as a function of age can be seen in the amounts of residual Jeffamine and BTDE and the higher molecular weight species designated imide and polymer 3. The elution volume of the low molecular weight imide corresponds to the elution volume of polystyrene of molecular weight 800; polymers 1, 2 and 3 correspond to polystyrene molecular weights of 1000, 2500 and 5000, respectively. BNI is a major reaction product whose concentration appears to be independent of resin age. LARC polymer is not completely cured after one hour at 140°C, as shown by the existence of BTDE and Jeffamine peaks

in the HPLC spectra (Fig. 10, Table VIII) and verified by the presence of unreacted BTDE in the  $^{13}\text{C}$ -NMR spectra. The Jeffamine, BTDE and imide peak areas all decrease and that of polymer 3 (the highest molecular weight species) increases with the age of the resin. These results show that aging the resin has the effect of partially advancing the reaction since more polymer and less Jeffamine and BTDE are observed under identical cure conditions with increasing age of the monomer mixture. Furthermore, aging the monomer resin mixture leads to the formation of slightly higher molecular weight polyimide chains after curing at  $140^\circ$  and  $180^\circ$ .

The increase in degree of cure at a given cure time and temperature for aged LARC monomer resin mixture is in contrast to effects of resin aging in the PMR system. Lauver has found that PMR resins containing the BTTE products formed during storage of alcohol solutions of PMR prepolymer require longer and higher temperatures to imidize.<sup>8-10</sup> In the LARC-160 system, however, we have shown that the nadic group reacts with time but that BTDE remains stable under the conditions of our experiments. The partial preimidization of the nadic group produces an advanced reaction state for the aged resin and when identical cure times are used for aged and fresh monomer mixtures, the older mixture has a higher average cured molecular weight.

### Conclusions

The composition of LARC-160 resin monomer mixture changes during aging at  $12^\circ\text{C}$ . The major effect of resin age is the formation of BNI, and the advancement of the nadimization reaction.

The NE and BTDE monomers imidize under different conditions. NE imidizes at  $12^\circ$  over a period of weeks and is completely imidized in a few minutes at



125°. No BTDE imidization was observed at 12°. Imidization of BTDE at 125° requires several hours, but is complete in 10 minutes at 180°.

Both NE and BTDE imidization reactions proceed directly to the imide. Neither amide is present in significant quantities during any stage of the imidization reaction, and is not a stable intermediate.

Aging the monomer resin mixture leads to the formation of slightly higher molecular weight polyimide chains after curing at 140° and 180°.

BNI is a major product of polymerization of LARC-160, regardless of resin age.

#### Acknowledgements

We wish to thank Dr. Melvyn D. Schiavelli for his patient instruction in the use of the Varian FT-80A NMR Spectrometer. This work was supported by Grant NSG-1095 from NASA, Langley Research Center.

Fig. 1. LARC-160 monomers:

BTDE = benzophenone tetracarboxylate, diethyl ester.

NE = ethyl-5-norbornene-2,3-dicarboxylate.

MDA = p,p'-methylene dianiline = Jeffamine,  $n = 0$ ,

Jef = Jeffamine, where  $n = 0, 1$  or  $2$ .

Fig. 2. LARC-160 monomer mixture, "cool-mix," 0.2% in THF, eluted from a  $2 \times 500 \text{ A}^\circ + 2 \times 100 \text{ A}^\circ$  column bank after the resin was stored at  $12^\circ\text{C}$  for the indicated number of days.

Fig. 3. LARC-160 monomer mixture, "warm-mix," 0.2% in THF, eluted from a  $2 \times 500 \text{ A}^\circ + 2 \times 100 \text{ A}^\circ$  column bank after resin was stored at  $12^\circ\text{C}$  for the indicated number of days.

Fig. 4.  $^{13}\text{C}$ -NMR spectrum of LARC-160 monomer mixture immediately after mixing. Solvent =  $\text{DMSO-d}_6$ ; k = benzophenone tetracarboxylate keto carbonyl; a = nadic imide carbonyl; b and c = nadic acid and ester carbonyls; e-h = benzophenone tetracarboxylic acid and ester carbonyls.

Fig. 5.  $^{13}\text{C}$ -NMR spectrum of LARC-160 monomer mixture after storage for six days at  $12^\circ\text{C}$ . d = nadic amide carbonyl; other assignments as in Fig. 4.

Fig. 6.  $^{13}\text{C}$ -NMR spectrum of LARC-160 monomer mixture after storage for 14 months at  $12^\circ\text{C}$ . Assignments as in Fig. 4.

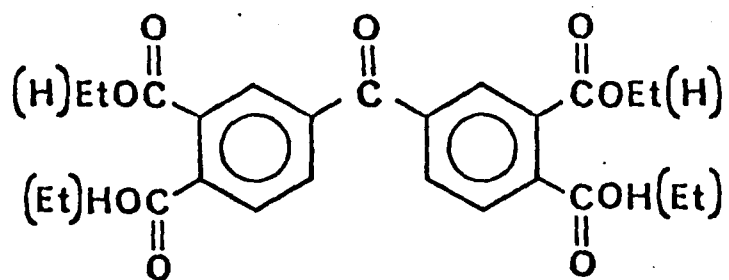
Fig. 7. HPLC spectra of LARC-160 cured at 180°C for times up to 60 minutes, 0.2% in THF with polystyrene - 51,000 added as an internal standard, eluted from a bank of 2 x 500 Å + 2 100 Å  $\mu$ -styragel columns.

Fig. 8. Infrared spectrum of fully imidized LARC-160 after curing 11 hours at 70°, 6 hours at 180° and 2 hours at 220°.

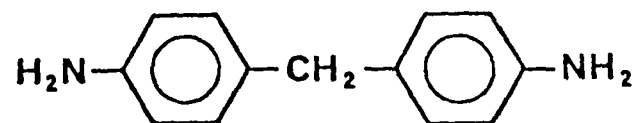
Fig. 9. HPLC spectra of LARC-160 cured at 180°C/1 hour from aging monomer mixture; 0.2% in  $\text{CHCl}_3$ , eluted from a five column bank consisting of 1 x 10<sup>3</sup> Å, 2 x 500 Å and 2 x 100 Å  $\mu$ -styragel columns. The monomer mixture was stored at 12°C for the indicated number of days before being cured.

Fig. 10. HPLC spectra of LARC-160 cured at 140°/1 hour from aging monomer mixture, 0.2% in THF, eluted from a bank of 2 x 500 Å + 2 x 100 Å  $\mu$ -styragel columns. The monomer mixture was stored at 12°C for the indicated number of days before being cured.

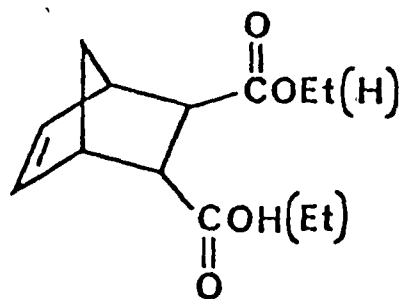
Fig. 1



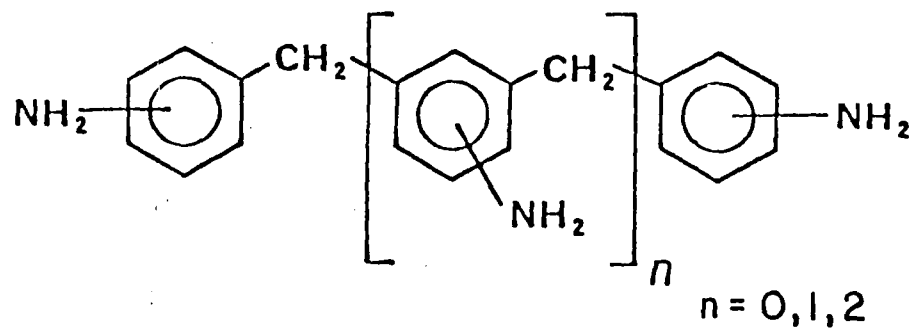
BTDE



MDA



NE



Jeffamine

Fig 2

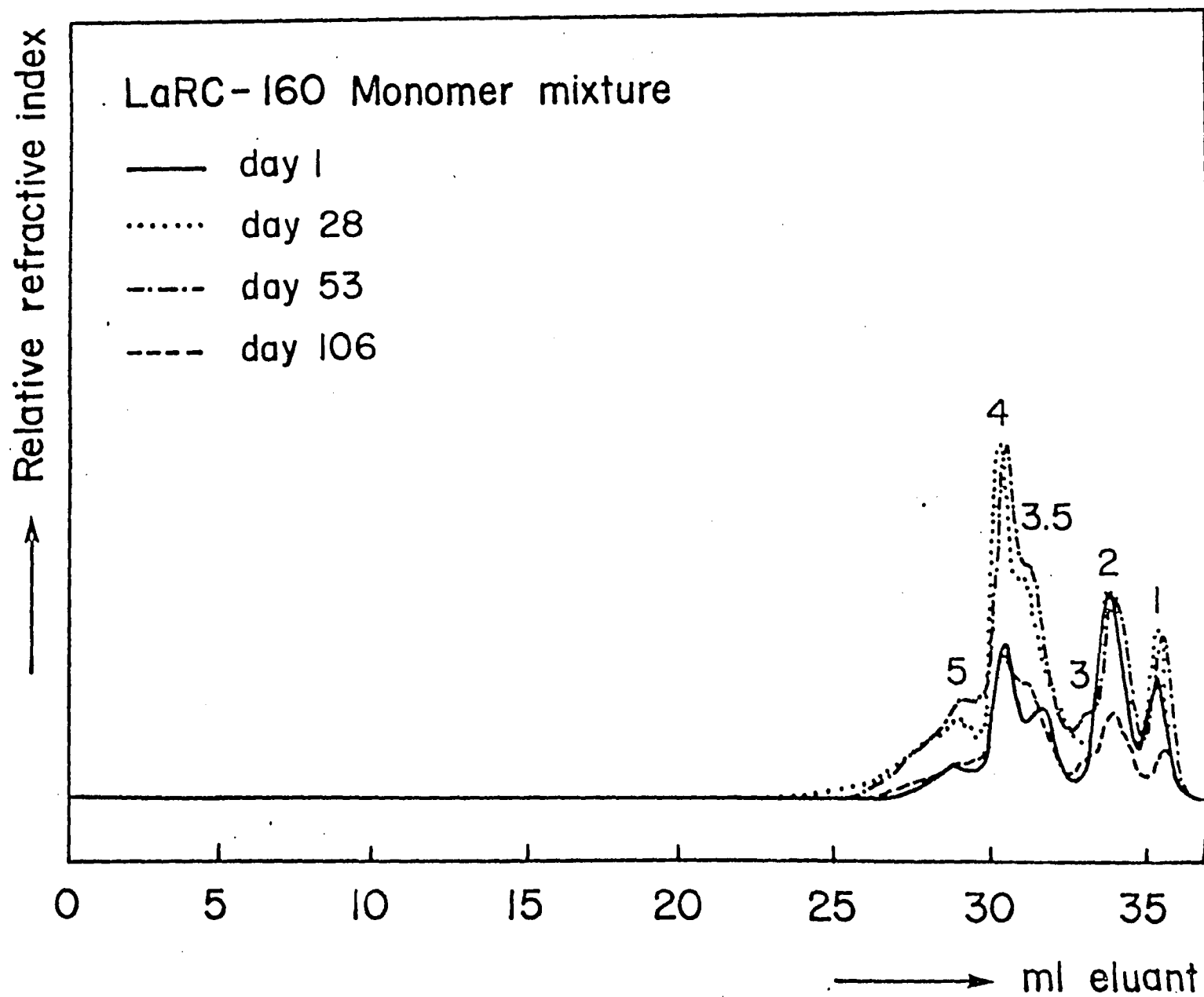
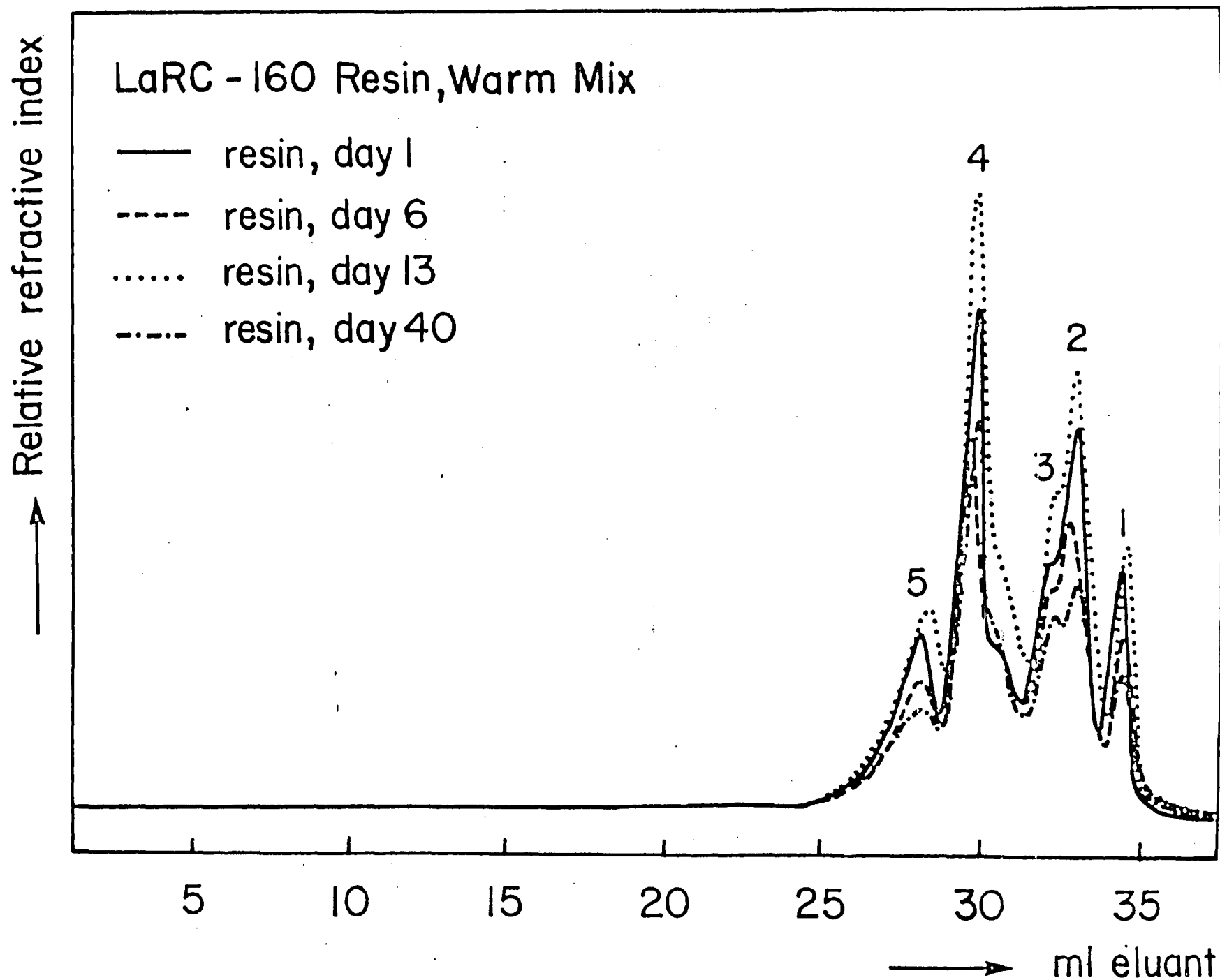


Fig 3



LaRC-160 Resin       $t = 1/2 - 3$  hrs at RT



Fig. 5

LaRC-I60 Resin  $t = 6$  days at  $12^{\circ}\text{C}$

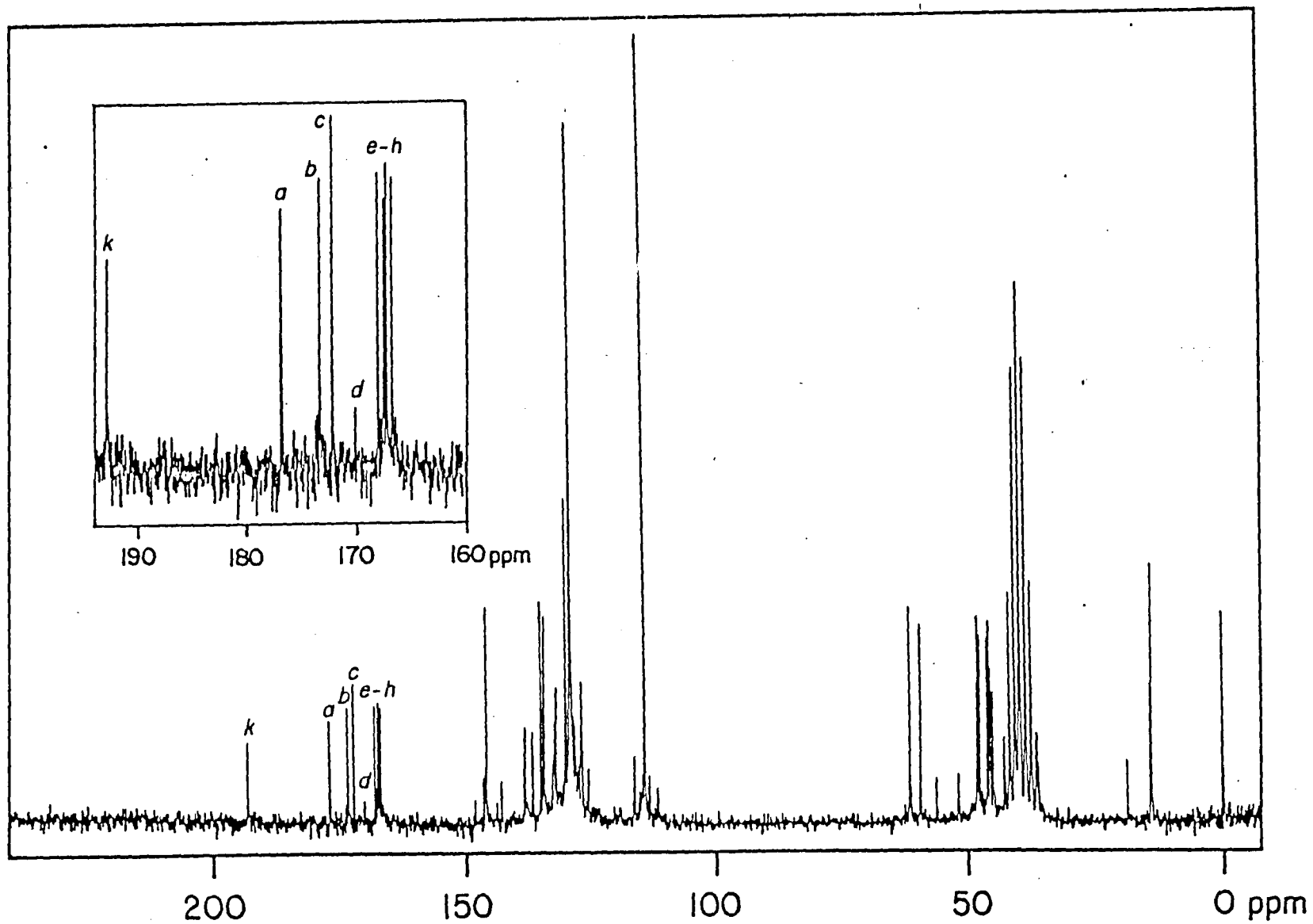




Fig. 6

LaRC-160 Resin  $t = 14$  months at  $12^{\circ}\text{C}$

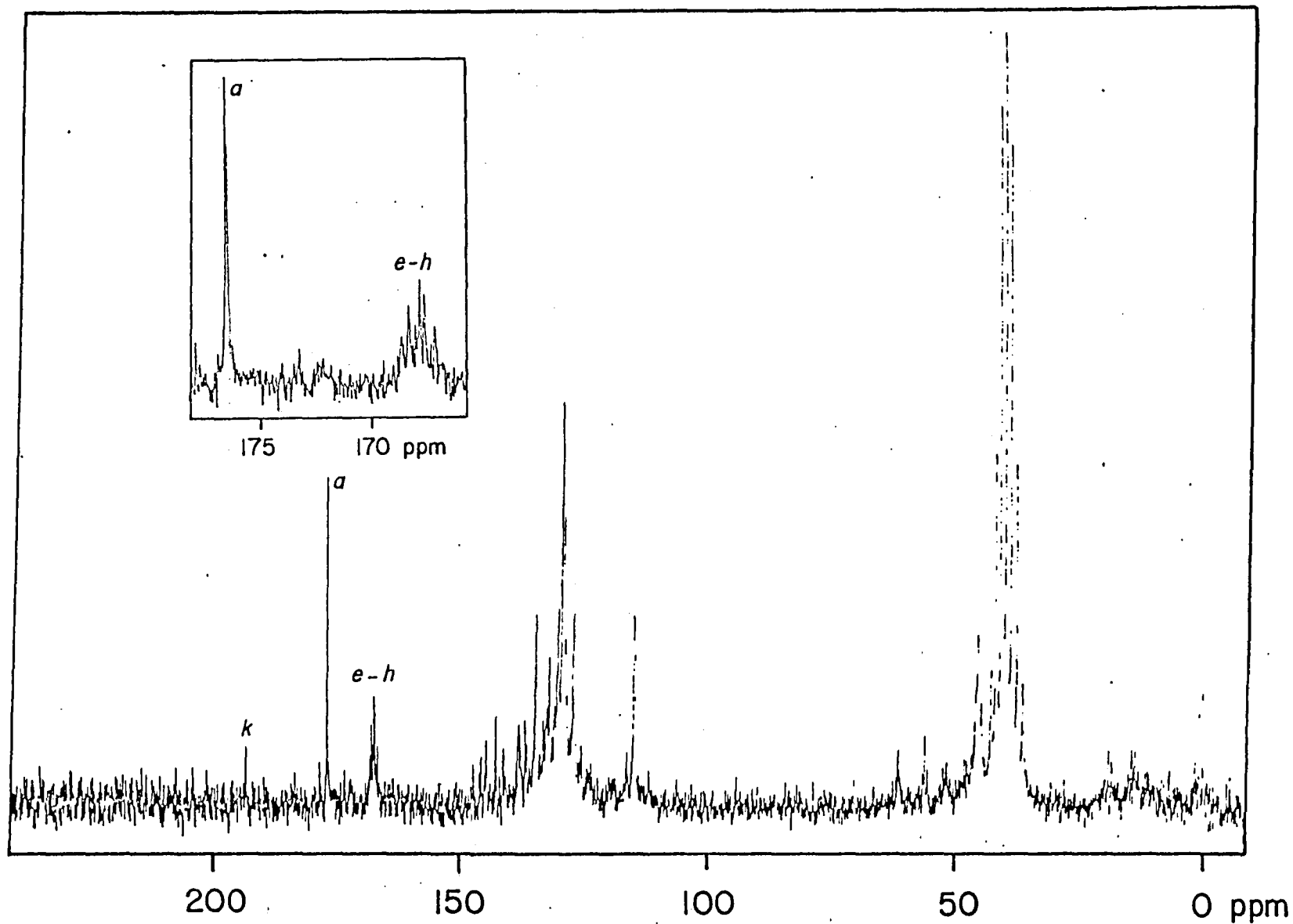


Fig. 7

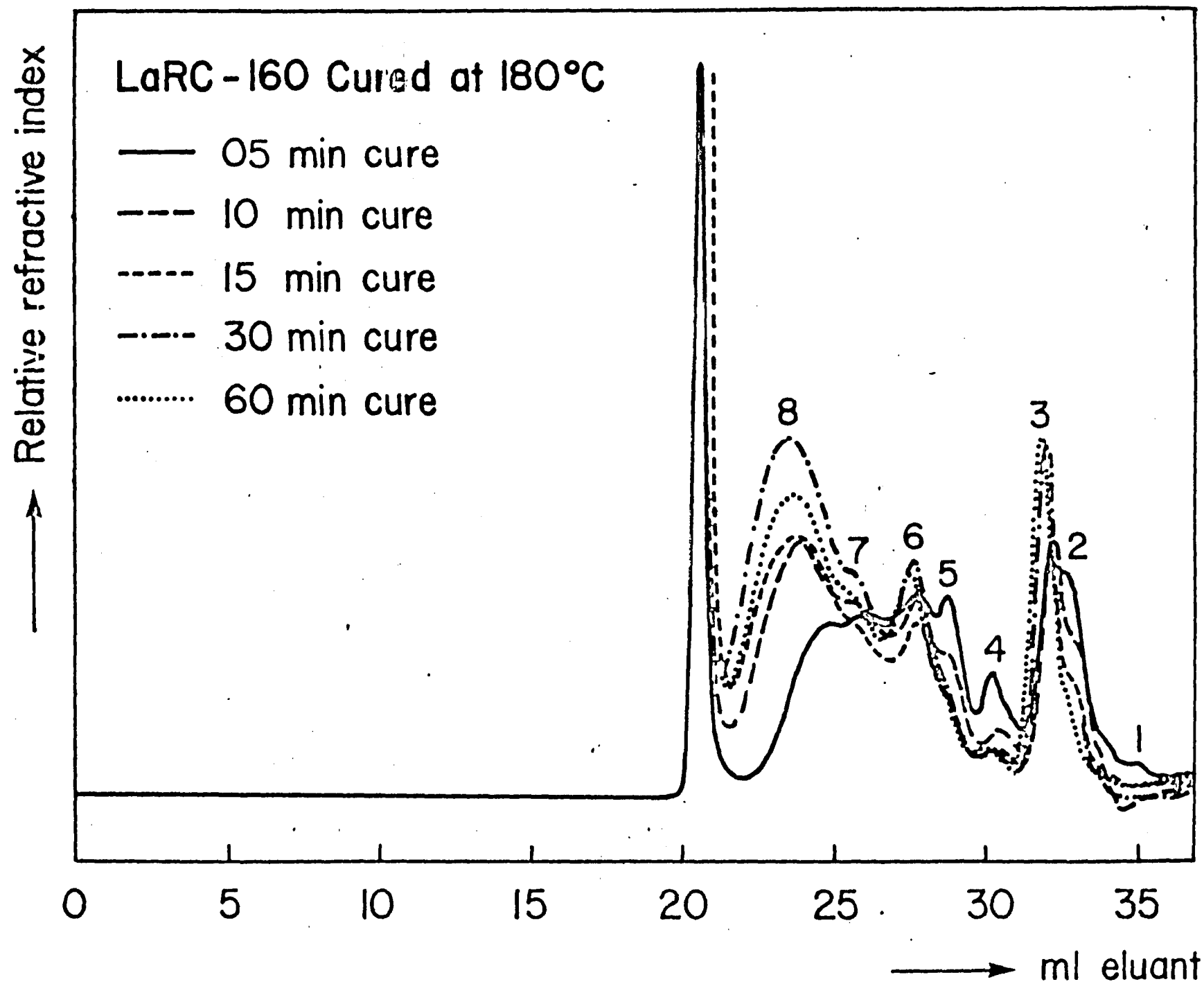


Fig. 8

LaRC-I60 cured 11 hrs at 70°, 6 hrs at 180°, and 2 hrs at 220°

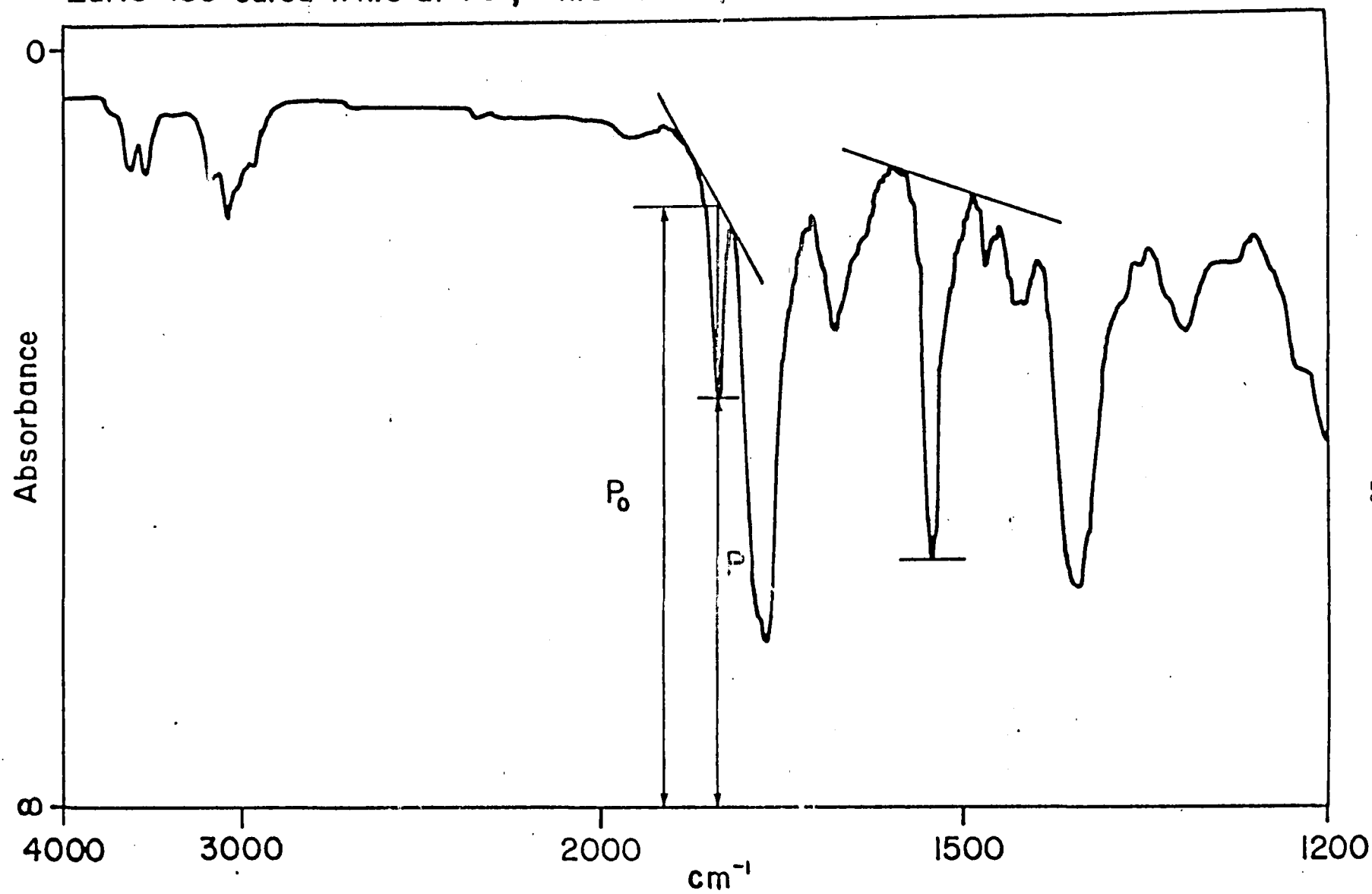


Fig. 9

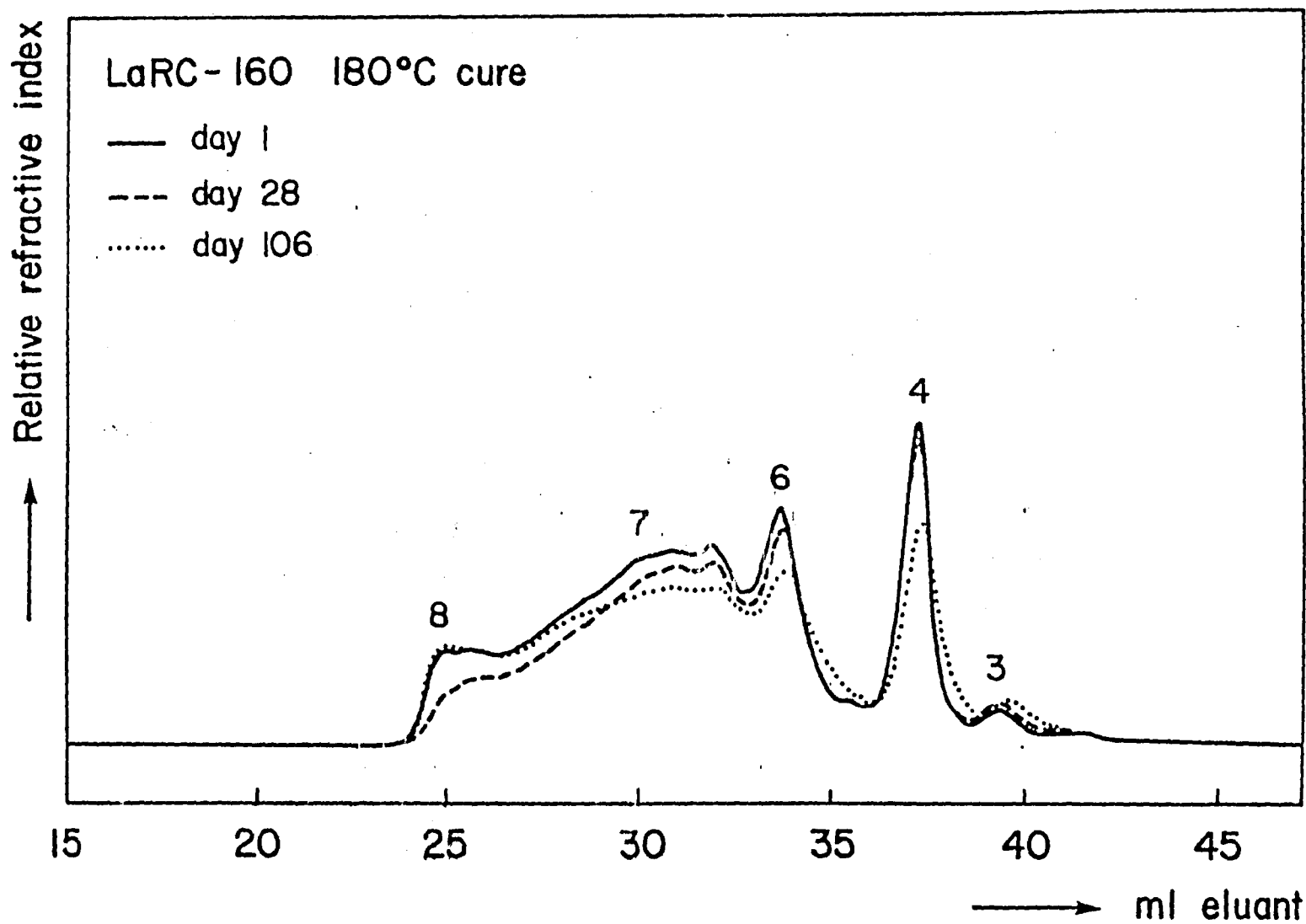


Fig. 10

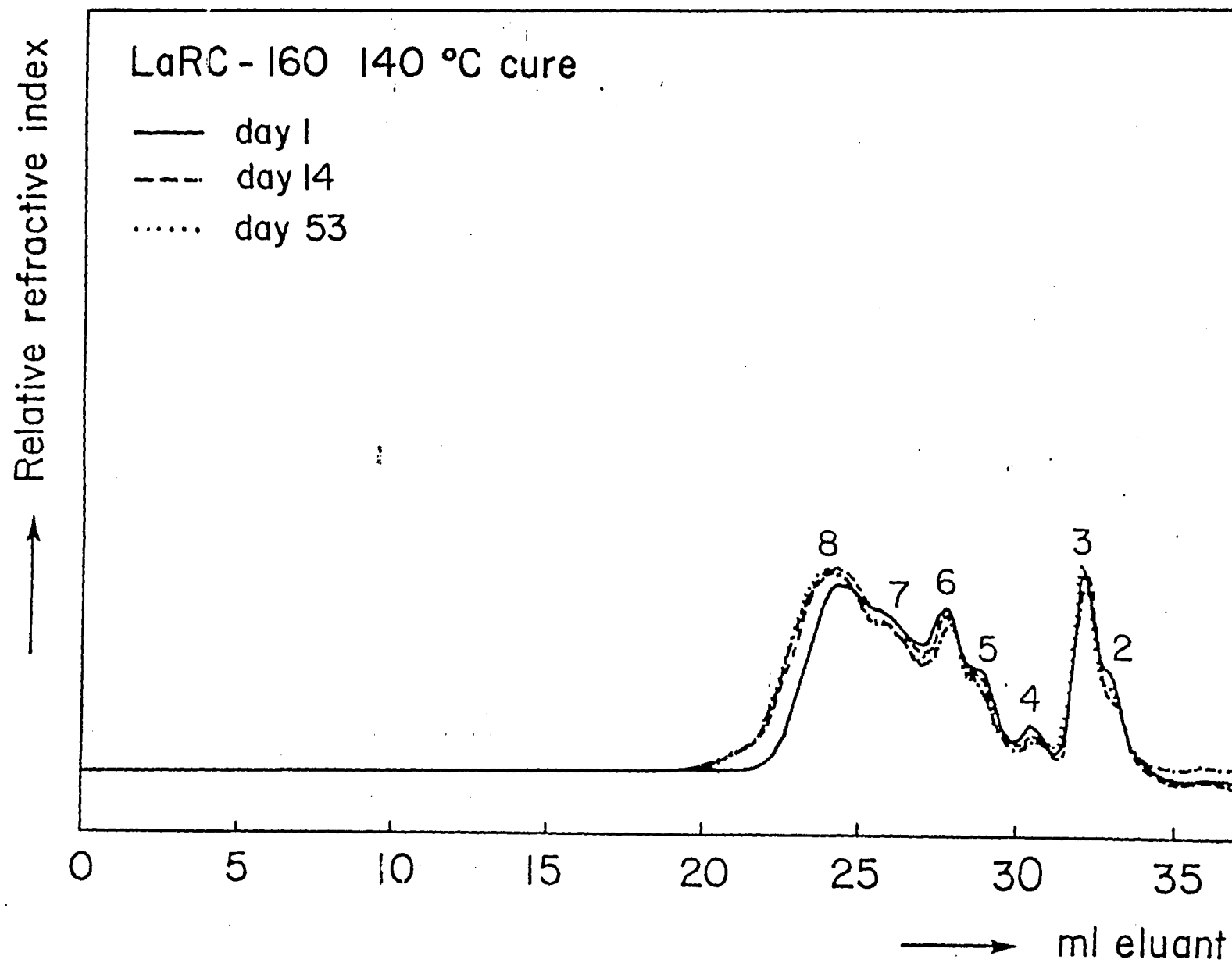


Table I HPLC Analysis of Aging LARC-160 Monomer Mixture, Cool Mix\*

Weight % after n days at 12°C										
Peak	Species	V <sub>e</sub> (±0.1 ml)	n = <u>1</u>	<u>7</u>	<u>14</u>	<u>28</u>	<u>53</u>	<u>106</u>	<u>287</u>	<u>377</u>
1	NE	35.2	31	28	26	22	14	13	13	0
2	Jeffamine, n=0	33.6	21	15	13	12	10	12	9	4 <sup>‡</sup>
3	Nadimide**	33.4	-	-	-	9	8	8	15	33 <sup>‡</sup>
3.5	Jeffamine, n=1	31.3	9	5	9	8	9	9	6	1 <sup>‡</sup>
4	BTDE	30.3	33	38	39	40	43	43	46	49
5	imide	28.9	6	13	13	10	16	15	13	13

\* 0.2% wt/wt in THF;  
two 500 Å° + two 100 Å°μ-styragel columns.

‡ Peaks 2,3 and 3.5 are inseparable. Jeffamine peaks are estimated based on the theoretical amount of Jeffamine left, assuming no BTDE has reacted.

\*\* In the unpolymerized mixture, both NI and BNI elute at this volume.

Table II    Percentage of Nadic Groups Reacted  
With Monomer Mixture Age as Determined  
From  $^{13}\text{C}$ -NMR Data

<u>age</u>	<u>% reacted</u>
1 hr	22
7 hr	22
15 hr	26
6 da	36
13 da	34
40 da	34
6 mo	73
14 mo	100

Table III HPLC Analysis of Aging LARC-160 Monomer Mixture, Warm Mix\*

Weight % after n days at 12°C								
Peak	Species	V <sub>e</sub> (±0.1 ml)	n = <u>1</u>	<u>6</u>	<u>13</u>	<u>19</u>	<u>34</u>	<u>40</u>
1	Nadic Ester	35.2	17	16	15	14	12	13
2	Jeffamine, n=0	33.6	13	13	13	12	11	10
3	Nadimide**	33.4	13	15	13	14	17	17
3.5	Jeffamine, n=1	31.3	6	6	5	6	4	9
4	BDTE	30.3	31	32	35	36	37	34
5	imide	28.9	20	19	18	20	19	16

\* Samples were 0.2% wt/wt in THF;  
two 500 Å° + two 100 Å°μ-styrigel columns.

\*\* In the unpolymerized mixture, both NI and BNI elute at this volume.



Table IV HPLC Analysis of "Warm-Mixed" LARC-160 after various cure times at 180°C\*

Peak	Species	V <sub>e</sub> (±0.1 ml)	x = 0	Weight % after x minutes at 180°C					
				5	10	15	20	30	60
1	Nadic Ester	35.2	16	2	-	-	-	-	-
2	Jeffamine, n=0	33.6	13	5	4	3	3	2	1
3	Bisnadimide	33.4	15	10	15	14	15	18	17
3.5	Jeffamine, n=1	31.3	6	-	-	-	-	-	-
4	BTDE	30.3	33	7	5	3	3	3	2
5	imide	28.7	17	21	8	6	4	5	5
6	Polymer 1	27.8		20	14	16	14	13	14
7	" 2	25.5		19	17	16	13	12	14
8	" 3	23.9		16	34	46	48	47	48

\* 0.2% wt/wt in THF;  
two 500 Å° + two 100 Å° μ-styragel columns.

Table V  $^{13}\text{C}$ -NMR Shifts of Observed Carbonyl Carbons of  
LARC-160 as a Function of Cure Time and Temperature

Cure Temp °C —	Cure Time (min)	a	b	c	e	f	g	h	i	j
12	0	176.73	173.16	171.96	167.72	167.15	166.94	166.44		
105	60	176.70			167.64	167.12	166.87	166.39	166.26	166.22
105	120	176.64				167.04		166.40	166.32	166.19
125	15	176.74	173.12	171.94	167.65	167.11	166.88	166.38		
125	30	176.64			167.57	167.07	166.81	166.42	166.34	166.23
180	5	176.70			167.59	167.04		166.40	166.33	166.19
180	10	176.61							166.32	166.18
180	30	176.63								166.19

\* Carbons a-h assigned as in Fig. 4; i = transient benzophenone tetracarboxylate amide;  
j = benzophenone tetracarboxylate imide.

Table VI Quantitative Analysis of Infrared Spectra of LARC-160 Resin  
Percent Imidization versus Cure Time

<u>Cure Time (min.)</u>	<u>Cure Temp (°C)</u>	<u>% Imidization</u>
0	70	0
10	70	-0.87
20	70	1.5
40	70	5.1
60	70	5.1
90	70	10
120	70	18
180	70	18
300	70	23
420	70	31
540	70	46
660	70	37
840	180	85
960	180	83
1020	180	83
1050	220	94
1110	220	89
1170	220	89
1290	220	99
1350	220	100

Table VII HPLC Analysis of Aging LARC-i60 Cured at 180° for 1 hr\*

<u>Peak</u>	<u>Species</u>	$V_e (\pm 0.1 \text{ ml})$	Weight % after n days at 12°C			
			n = <u>1</u>	<u>28</u>	<u>53</u>	<u>106</u>
4	BTDE	40	2.9	4.7	2.7	2.6
3	Bisnadimide	37.7	22.1	22.9	21.3	19.9
6	Polymer 1	34.1	17.9	19.8	16.8	16.7
7	" 2	30	48.4	44.4	48.2	48.0
8	" 3	25.5	8.7	8.1	11.0	12.8

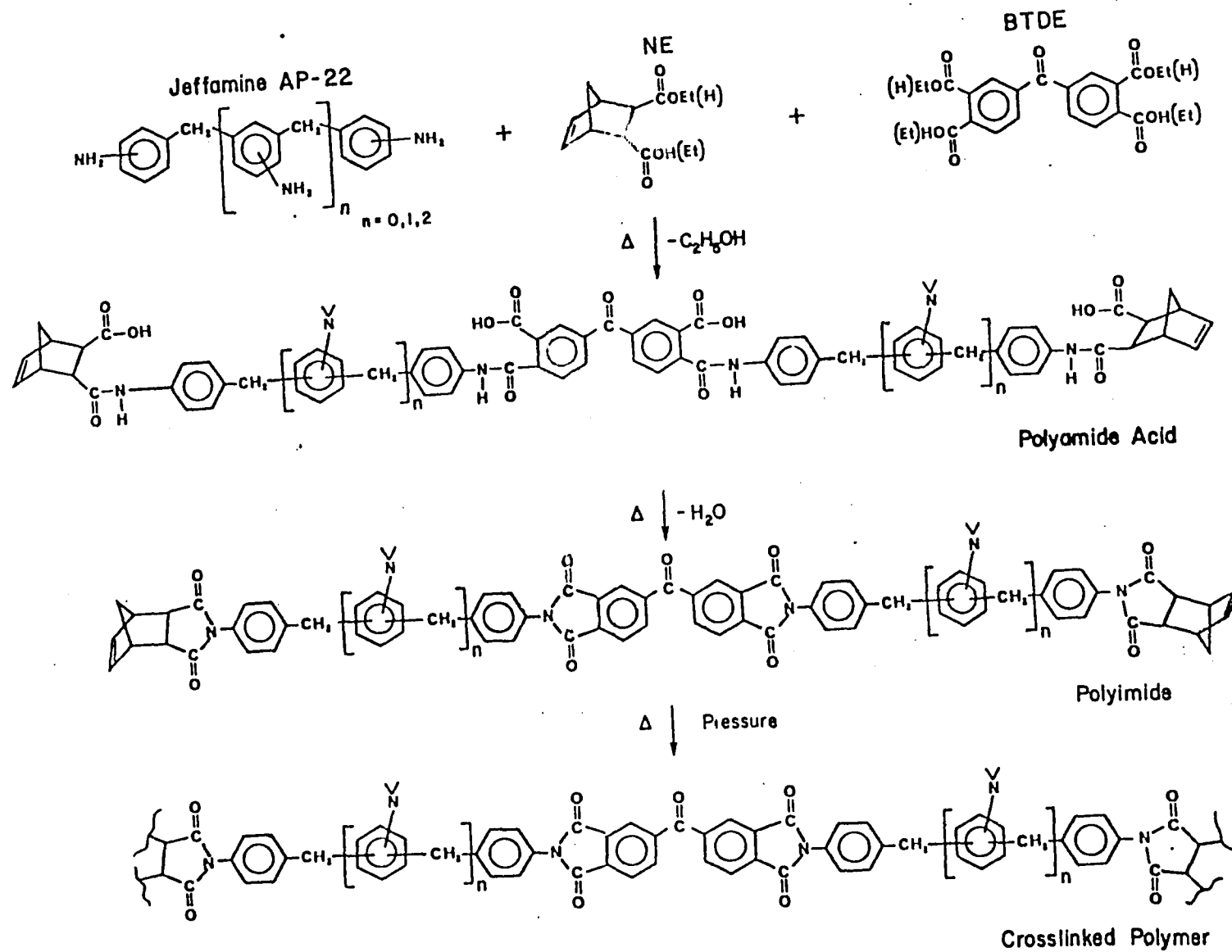
\* 0.2% wt/wt in  $\text{CHCl}_3$  ;

one  $10^3 \text{ A}^\circ$  + two  $500 \text{ A}^\circ$  + two  $100 \text{ A}^\circ \mu$ -styrigel columns. .

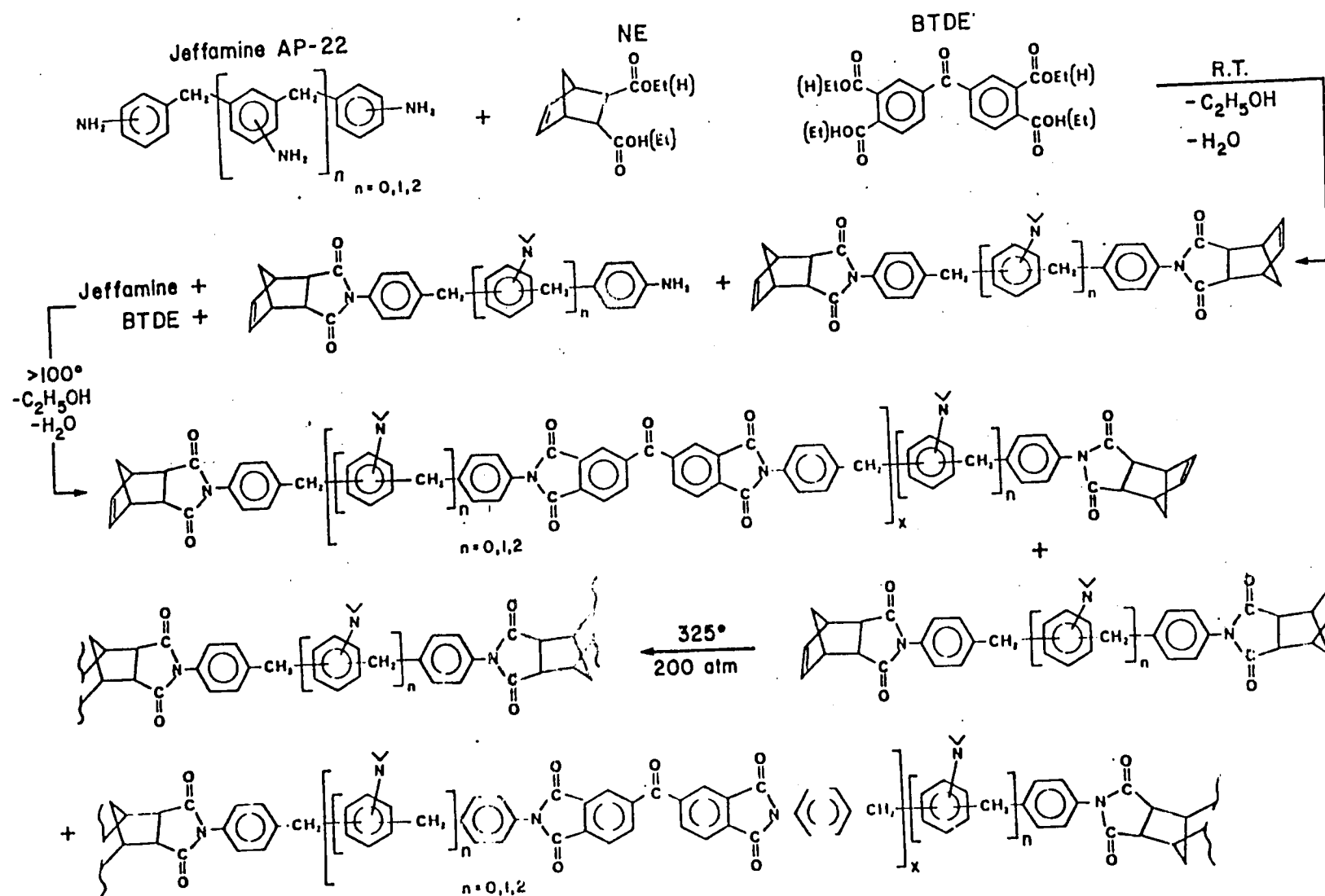
Table VIII HPLC Analysis of Aging LARC-160 Cured at 140° for 1 hour\*

Weight % after n days at 12°C									
Peak	Species	V <sub>e</sub> (±0.1 ml)	n = <u>1</u>	<u>4</u>	<u>7</u>	<u>14</u>	<u>28</u>	<u>53</u>	<u>106</u>
2	Jeffamine, n=0	33.0	4	3	3	3	3	2	2
3	Bisnadimide	32.3	19	18	17	16	16	17	17
4	BTDE	30.5	5	6	6	6	5	5	2
5	imide	28.7	8	8	8	7	8	6	5
6	Polymer 1	27.8	18	16	17	15	15	15	16
7	" 2	25.5	13	16	17	15	17	14	17
8	" 3	24.3	33	34	34	38	38	43	41

\* 0.2% wt/wt in THF  
two 500 Å + two 100 Å $\mu$ -styrigel columns.



SCHEME I



SCHEME II

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## Part B

## Kinetic Studies on Degradation in Polyimide

## Precursor Resins

Aromatic polyimides, those with aromatic groups in their backbone, have generated considerable interest in recent years because of their thermal and thermooxidative stability. They have considerable utility in air between 200-300°C and are usable for short periods of time at 400-500°C<sup>1,2</sup>. They are therefore being considered for use as structural composites in the National Aeronautics and Space Administration space shuttle program. On the other hand, the high glass transition temperature of polyimides makes processing difficult. As a result, the acid and amine monomers are often polymerized in solution to form a polyamic resin. This polyimide precursor resin solution may be applied to a fiber backing and cured at a high temperature to form a thermally stable polyimide composite. While the effect of chemical structure on the thermooxidative and thermomechanical properties of the cured polyimide resin has been studied<sup>1-4</sup>, very limited kinetic information is available on the stability of the polyamide resin<sup>5</sup>.

## Experimental

A series of 15% by weight isomeric polyimide precursor resin solutions was prepared at the NASA Langley Research Center. The polymerization procedure has been described previously<sup>1</sup>. The polyamic resins were made from 3,3',4,4' benzophenone tetracarboxylic acid dianhydride (BTDA), 4,4' oxydiphthalic anhydride (ODPA), diaminobenzophenone (DABP) and methylene dianiline (MDA) monomers. The solvent dimethylacetamide was distilled from calcium hydride under vacuum and stored over nitrogen. The resin solutions were also stored under nitrogen. The water content of the solvent was measured with a Porapak Q column in a Hewlett Packard 5750 gas chromatograph. Unless otherwise stated, the water concentration in the solvent was maintained below 0.05 volume percent.

The number average molecular weight  $\bar{M}_n$  was determined from osmotic pressure measurements on a Hewlett Packard-Mechrolab 502 osmometer. ArRo Lab gel cellophane 600D membranes were used.

## Results and Discussion

The change in  $\bar{M}_n$  due to degradation of the resin solution was observed as a function of time for 22 to 52 day periods or until  $\bar{M}_n$  fell below 5000. Assuming degradation occurs by random scission and that the initial fraction of functional groups reacted,  $p_0$  undergoes little change,

$$\frac{1}{\bar{M}_n(t)} = \frac{1}{\bar{M}_n(o)} + \frac{kp_0t}{M_0}$$

where  $M_0$  is the molecular weight of a monomer unit. The rate constant  $k$  was determined from a least squares fit of  $1/\bar{M}_n(t)$  versus time. The maximum deviation from the least squares fit was 6% for  $\bar{M}_n > 10,000$  and 8% for  $10,000 > \bar{M}_n > 5,000$ . The uncertainty in  $k$ , based on measurements of several different polymerization batches, is estimated to be 20%.

Table I lists values of  $k$  for a series of polyimide precursor resins. The data show that the DABP resin solutions are more stable than their MDA counterparts. For both the DABP and the MDA polymers, the para amide linkage was more stable than the meta or ortho structure. It was anticipated that the stability would be correlated with the basicity of the diamine. Indeed, methyl substituted anilines have a  $pK_a$  which is two more than methyl carbonyl substituted anilines<sup>6</sup>. However, the  $pK_a$  of methyl substituted anilines shows a small increase in basicity in going from the ortho to the para isomer<sup>6</sup>. Thus, while the rate of degradation may be affected by the basicity of the amine, Table I suggests that  $k$  is more strongly dependent on the geometric linkage at the amide bond.

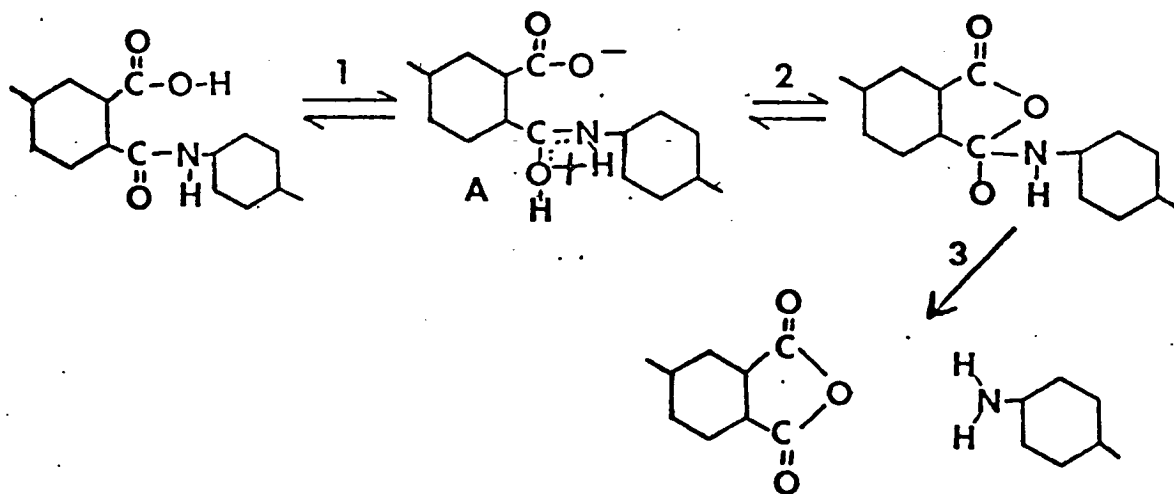
The effect of the presence of water in the solvent on the

stability of the resin is shown in Table I. The observed linear relationship indicates that  $k$  is proportional to the water concentration. From a plot of  $k$  versus %H<sub>2</sub>O, the slope of the three point line is  $0.075 \times 10^{-4}$  and the intercept  $k$  (anhydrous) is  $0.031 \times 10^{-4} \text{ days}^{-1}$ , in good agreement with the nearly anhydrous  $k(\text{H}_2\text{O} < .05\%)$  value of  $0.032 \times 10^{-4} \text{ days}^{-1}$ .

Only limited data on the temperature dependence of  $k$  has been obtained. The approximate values for the activation energy fall within the range of 15 to 30 kcal normally observed in amide hydrolysis.

Increasing the concentration of the resin solution from less than 0.6 to 7.5 and 15 weight percent polymer decreased the rate of degradation.

The hydrolysis rate of phthalamic acid is  $10^5$  times faster than that of benzamide. Formation of a phthalic anhydride intermediate has been demonstrated in C<sup>13</sup> and O<sup>18</sup> labeling experiments<sup>6</sup>. These results and the degradation data are consistent with the previously proposed mechanism of intramolecular displacement by the carboxylate anion on the protonated amide<sup>5,7,8</sup>.



Electron donating groups between the phthalic acid groups such as

in ODPA m,m' MDA move the equilibrium (1) to the left. The formation of a tetrahedral intermediate is also consistent with the dependence of  $k$  on the geometric structure of the amide linkage. The basis for the polymer and the water concentration dependence is not as clear. Attack by water on the protonated amide (A) may compete with the proposed intramolecular degradation process. Water would also hydrolyse phthalic anhydride, making it less likely to recombine with the amine in step (3).

## Conclusions

The number average molecular weight of the polyimide precursor resins dropped to half the original value in 14 to 90 days when stored under anhydrous conditions at room temperature. The rate of degradation was sensitive to the presence of water and was dependent on the geometric nature of the amide linkage. Increasing the concentration of the resin solution and the presence of an electron donating group between the phthalic acid groups increased the stability. Those factors which affect  $T_g$  and the reactivity of the monomers<sup>1,2</sup> were not directly related to the stability of the resin solution, suggesting that the properties of polyimides may be optimized by varying their chemical structure.

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TABLE I Rates of Degradation

Compound	v/v% $H_2O$	Wt.%Polymer	Temp.	$\frac{kp_0}{M_0} (x10^4 \text{ days})$
BTDA m,m' DABP	<.05	<0.6	27	.032
BTDA p,p' DABP	<.05	<0.6	27	.0096
BTDA o,p' MDA	<.05	<0.6	27	.057
BTDA m,m' MDA	<.05	<0.6	27	.044
BTDA p,p' MDA	<.05	<0.6	27	.021
ODPA m,m' MDA	<.05	<0.6	27	.0081
BTDA p,p' DABP	<.05	<0.6	40	.060
BTDA m,m' MDA	<.05	<0.6	35	.092
BTDA p,p' MDA	<.05	<0.6	40	.102
BTDA m,m' DABP	0.10	<0.6	27	.038
BTDA m,m' DABP	0.30	<0.6	27	.053
BTDA m,m' DABP	0.50	<0.6	27	.068
BTDA m,m' MDA	<.05	7.5	27	.028
BTDA m,m' MDA	<.05	15.0	27	.021

\*The value of  $p_0$  was .95 to .96 for the BTDA - DABP polymers and .97 to .98 for the BTDA - MDA and ODPA - MDA polymers.

## Part C

Relationship of Cure Conditions to Solubility and  
Glass Transition Temperature

Polyimides with aromatic groups in their backbone have generated considerable interest as matrix resins for high performance composites because of their thermal and thermooxidative stability. On the other hand, the high glass transition temperatures of polyimides make processing difficult. Therefore, the polyimides are processed by either (1) making a linear poly(amic-acid) resin and then imidizing to form a predominantly linear polymer or by (2) making short imide chains which are end capped with nadic groups and then crosslinking the nadic groups in an addition reaction. With the second processing approach, the cure conditions are the major factor which determines the glass transition temperature. The relationship of the cure conditions on the glass transition temperature<sup>1</sup> of crosslinked nadic polyimides, process (2), has been examined.

Glass transition temperature and the solubility of crosslinked nadic polyimides were examined for two systems. The first was solventless LARC-160, and the other was PMR. Both the PMR and LARC-160 resins were used as received from the NASA Langely Research Center. Both of these resin systems consist of a mixture of the diethyl ester of benzophenone tetracarboxylic acid (BTDE), and the ethyl ester of norbornene dicarboxylic acid (NE) and methylene dianiline (MDA). The LARC-160 differs from the PMR resin in that LARC-160 contains, in addition to bifunctional MDA isomers, trifunctional aromatic amines.



The LARC-160 and PMR resins are processed in general in two steps as shown in figures 1 and 2. The first step is a condensation reaction to form a polyimide in which the oligomers are end-capped with the nadic group. In the second step, which is conducted at a higher temperature and under pressure, these short chain polyimides undergo an addition reaction of the nadic group which ties the chains together to form a cross-linked structure.

Table 1 shows the relationship of the cure temperature on the percent solubility and the glass transition temperature of the cured polymer for both the PMR and LARC-160 systems. In both systems, after having cured the polymer at 200 degrees for an hour or more, the resin formed an amorphous rubbery solid, almost all of which would dissolve in dimethylacetamide after stirring at 50 degrees for one hour. The fact that the material softened as it was heated and that the polymer was slightly soluble supports the view that curing up to 200 degrees results in a condensation reaction in which short chain predominantly linear oligomers are formed. For both systems subsequent cures at 240, 280 and 325 degrees have a marked effect on the solubility and the glass transition temperature. After curing at 280 degrees little of the polymer dissolved and a moderately high glass transition temperature was measured. When the polymer was cured at 325 degrees, virtually all of the polymer was insoluble and the glass transition temperature was over 300 degrees. The insolubility of the polymer and the high glass transition temperature suggest that a cross-linking reaction has taken place. The information in Table 1 suggests that the precise temperature at which the addition reaction

takes place is different in the LARC-160 and PMR systems. The solubility data suggest that in the PMR system the addition reaction has occurred at 280 degrees. For the LARC-160, after curing at 280 degrees, the higher percent solubility and a lower glass transition temperature suggest that the crosslinking density is lower. It is interesting to note that for the PMR and LARC-160 systems after the 325 degree cure, both systems have a glass transition temperature which is close to the temperature of the final cure process; that is the 332 and 318 degree values for the glass transition temperature are quite close to the 325 degree temperature at which both systems were cured.

The observation that the glass transition temperature for a crosslinked system may be directly dependent upon the temperature of the final cure has been fully developed in a series of papers by J. K. Gillham. Figure 3, which has been taken from Gillham's work, is a plot of the time to gelation and to vitrification versus the cure temperature. This graph can be conveniently used to describe the conditions under which one would expect the glass transition temperature to be dependent upon the final cure temperature. Figure 3 is divided into three regions. In the first region, designated by the letter A, the resin is cured at a temperature which is below the temperature at which the resin would gel,  $T_{gg}$ . A knowledge of  $T_{gg}$  is important because the polymer resin should be stored at a temperature below  $T_{gg}$  to prevent crosslinking. In region B, the polymer is cured at a final cure temperature which is greater than the temperature at which gelation occurs.

For polymers cured at a temperature greater than  $T_{gg}$ , the polymer goes from a fluid resin to a rubbery state and then finally vitrifies. Region C represents a cure condition in which the final cure temperature exceeds the maximum value of the glass transition temperature  $T_{g\infty}$  for the polymer. In this region the polymer resin goes from the fluid state to a rubbery state, but never vitrifies.

Region B is characterized by two phenomena. First the time to gelation decays exponentially as the cure temperature increases. This is due to the Arrhenius dependence of the rate of the reaction on temperature. Second, the functional dependence of the time to vitrification versus cure temperature decreases, goes through a minimum, and then increases rapidly up to an exponential limit which is characterized by  $T_{g\infty}$ . The minimum in the plot of temperature versus time for vitrification reflects the competition between the increase in the reaction rate with temperature as opposed to the increased degree of crosslinking needed to form a glass at higher temperatures. The final point to be noted in region B is that once vitrification occurs the reaction is essentially quenched. Since as a glass the polymer molecules have no translational mobility and limited mobility about segments within the polymer chain.

When the resin is cured at a temperature between  $T_{gg}$  and  $T_{g\infty}$ , region B, the oligomeric chains join together until one reaches the gel point. At this point the polymer becomes rubbery; the crosslinking reaction is nevertheless not 100% complete. The degree of crosslinking continues to increase

until it reaches a sufficient degree for the polymer to form a glass. If this process is repeated at a higher cure temperature, but nevertheless at a temperature between  $T_{gg}$  and  $T_{g\infty}$ , a higher crosslinking density is needed before vitrification occurs, because the temperature is higher. Once the crosslink density becomes sufficiently high, higher than in the first case, the polymer again forms a glass. Thus, when a polymer is cured at a cure temperature between  $T_{gg}$  and  $T_{g\infty}$  the value of the cure temperature determines the glass transition temperature. If one wants to increase the glass transition temperature, one need only take the polymer and post cure it at a higher temperature. The higher post cure temperature turns the polymer from a glass into a rubbery state, the crosslinking reaction continues, the crosslink density continues to rise until the crosslink density becomes sufficiently high to form a glass at the higher post cure temperature. As a result the glass transition temperature should be linearly dependent on the cure temperature.

Table 2 lists the value of the glass transition temperature for LARC-160 as a function of the final cure temperature over a range of values from 240 degrees to 440 degrees Centigrade. As shown on Table 2: once the final cure temperature reaches 325 degrees, the final cure temperature is equal to the value of the glass transition temperature within experimental error. Figure 4 shows a plot of the glass transition temperature versus the cure

temperature. A linear relationship between the cure temperature and glass transition temperature for LARC-160 at cure temperatures greater than 325 degrees Centigrade is observed.

The percent solubility data and the glass transition temperature data suggest that for PMR the value of  $T_{gg}$  is between 200 and 250 degrees. For the LARC-160 system the value of  $T_{gg}$  appears to be slightly higher. The value of  $T_{g\infty}$  could not be determined because the polymers decomposed when post cured at temperatures exceeding 440 degrees. The data suggest that for structures made out of LARC-160 or PMR the value of the glass transition temperature will be linearly dependent on the final temperature used in the post cure operation. Thus, if an exceptionally high glass transition temperature is required, the LARC-160 or PMR structures should be post cured at a temperature greater than the glass transition temperature required.

1

The value of the glass transition temperatures was determined at NASA Langley using a mechanical probe. The phrase "glass transition temperature" is used loosely, since a measurement was actually made on the softening temperature, that is, the temperature at which a probe with a nominal weight penetrated the material.

Table 1

Effect of Cure Conditions on % Solubility and  $T_g$ LARC 160  
(SOLVENTLESS)

CURE CONDITIONS	% SOLUBILITY	$T_g$
3 HRS @ 200°C	97	
3 HRS @ 200°C, 2 HR @ 240°C AT 100 PSI	98	138°C
3 HRS @ 200°C, 1 HR @ 280°C AT 100 PSI	23	196°C
3 HRS @ 200°C, 1 HR @ 325°C AT 100 PSI	.1	332°C

PMR

CURE CONDITIONS	% SOLUBILITY	$T_g$
1 HR @ 100°, 140°, 170°, 200°	97	
1 HR @ 100°, 140°, 170°, 200°, 240°+ 100 PSI	45	224°
1 HR @ 100°, 140°, 170°, 200°, 280°+ 100 PSI	1	279°
1 HR @ 100°, 140°, 170°, 200°, 325°+ 100 PSI	.2	318°

Table 2

## POST CURE DATA

LARC - 160

CURE CONDITIONS	T <sub>g</sub>
3 HRS @ 200°, 2 HRS @ 240° + 100 PSI	136°
3 HRS @ 200°, 2 HRS @ 280° + 100 PSI	183°
3 HRS @ 200°, 2 HRS @ 325° + 100 PSI	313°
3 HRS @ 200°, 2 HRS @ 280° + 100 PSI, 1 HR @ 360°	352°
1 HR @ 200°, 1 HR @ 325° + 100 PSI, 1 HR @ 390°	375°
1 HR @ 200°, 1 HR @ 325° + 100 PSI, 1 HR @ 410°	437°
1 HR @ 200°, 1 HR @ 325° + 100 PSI, 1 HR @ 430°	433°
3 HRS @ 200°, 2 HRS @ 280° + 100 PSI, 1 HR @ 440°	460°

Figure 1

## LARC-160 PREPARATION

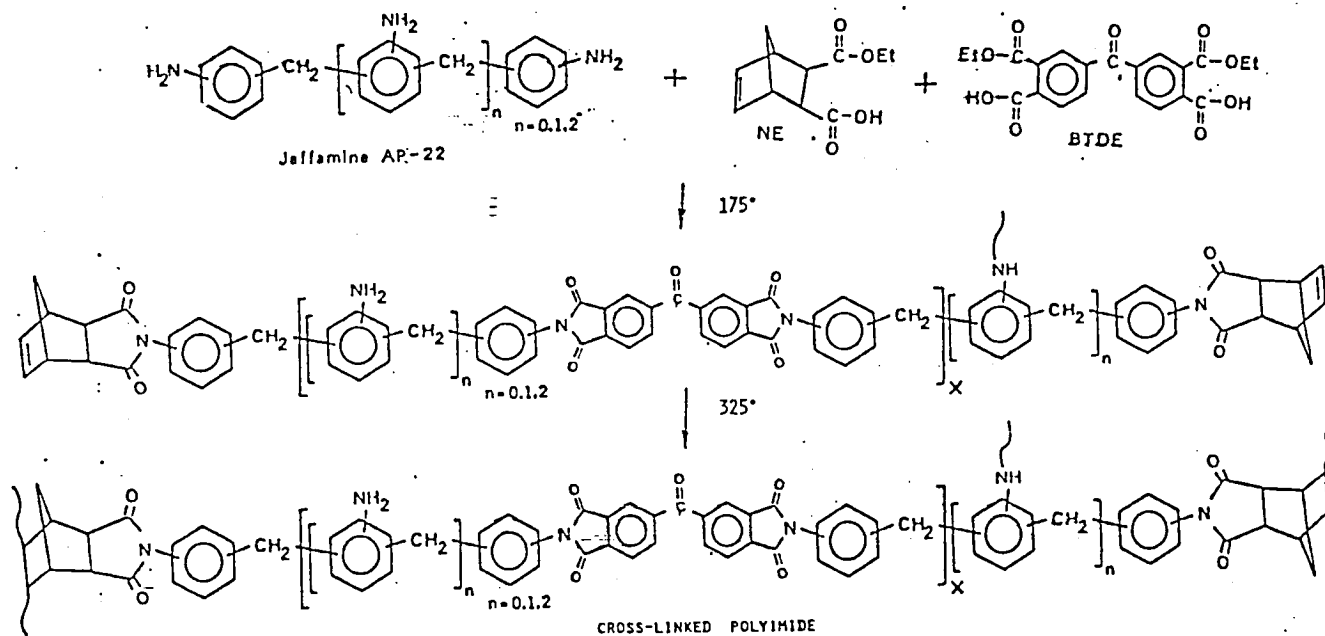




Figure 2

## PMR APPROACH

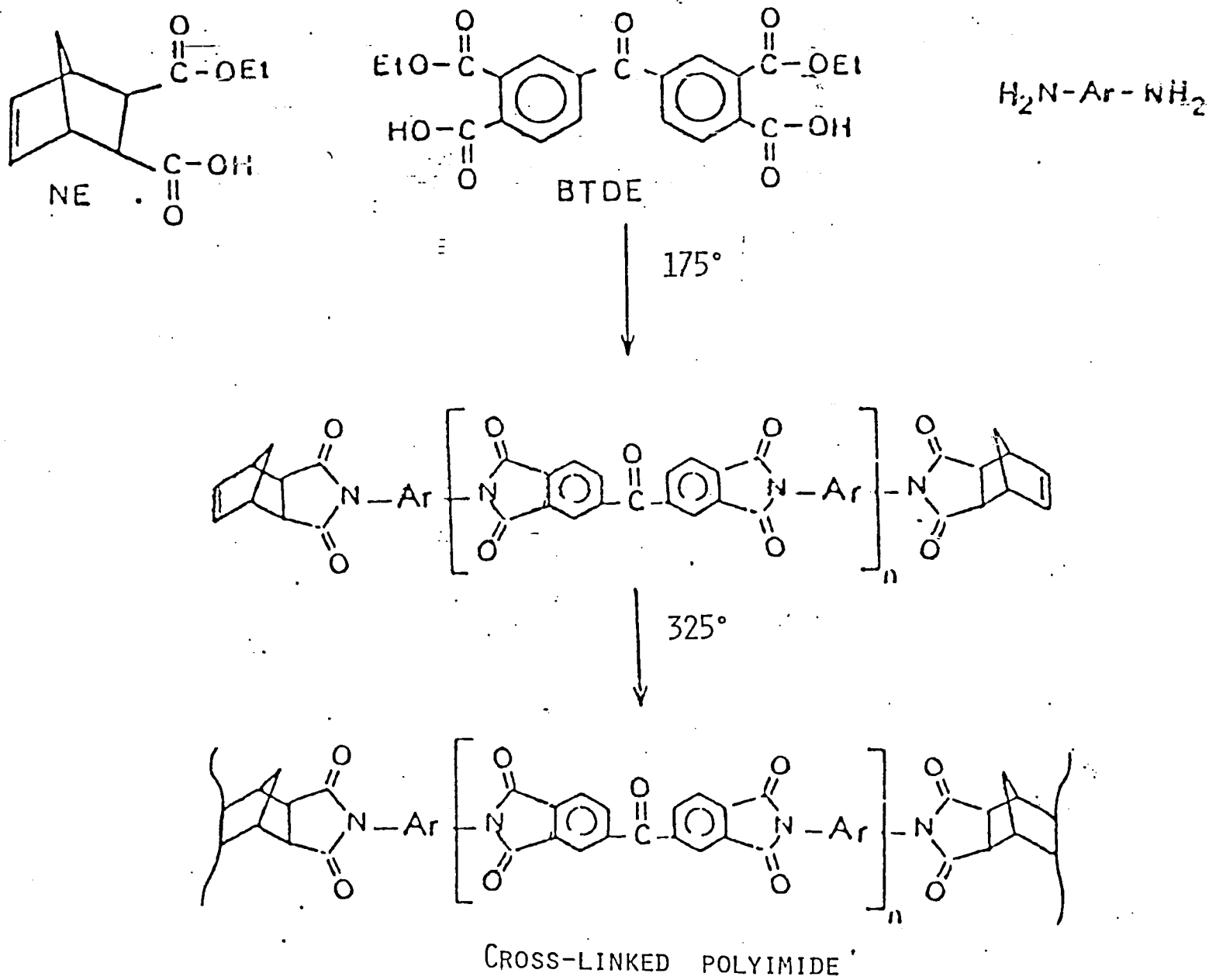


Figure 3

TRANSFORMATION  
FROM THE FLUID  
TO THE GLASSY  
STATE BEFORE  
THE ONSET OF  
GELATION

TRANSFORMATION  
FROM THE FLUID  
TO THE RUBBERY  
STATE AND THEN  
TO A GLASS

THE MAXIMUM  
GLASS TRANSITION  
TEMPERATURE IS  
EXCEEDED AND THE  
POLYMER DOES NOT  
FOR A GLASS BUT  
REMAINS A RUBBER  
AT THESE TEMPERA-  
TURES

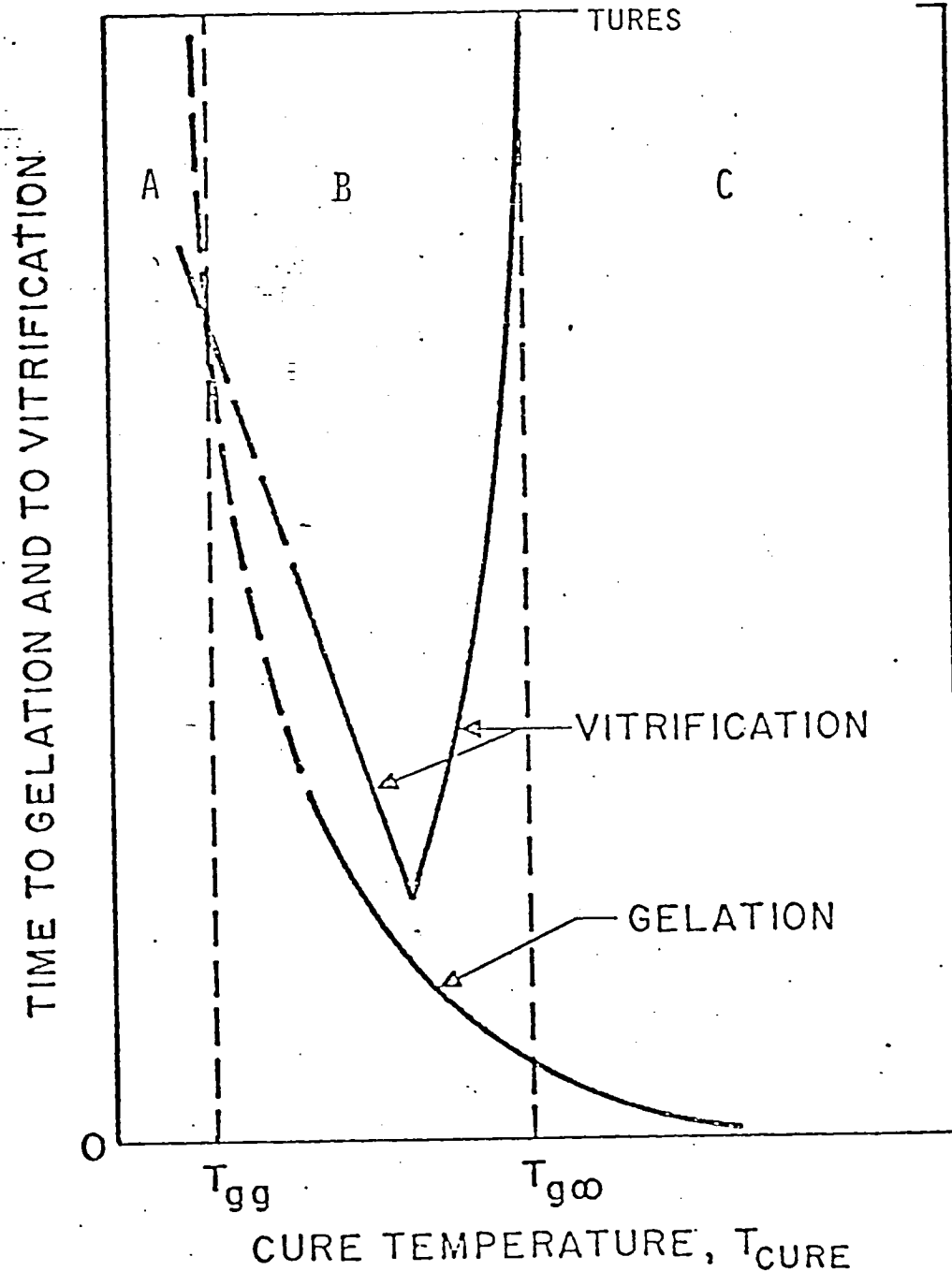


Figure 4

